

Correlation between magnetostriction and polarization in orthorhombic manganites

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Abstract. Recently we have reported the observation of colossal magnetostriction effect in HoMn_2O_5 single crystals. Besides we have made the supposition for possible correlation between the peculiarities, observed in the field depended polarization measurements, and the colossal magnetostriction effect at a 4.2 K temperature. In this article we present our results received by polarization and magnetostriction measurements on HoMn_2O_5 and TbMn_2O_5 single crystals and the strong correlation between magnetostriction and polarization phase transition for these two compounds. The origin of this correlation is discussed.

PACS. 75.80.+q Magnetomechanical and magnetoelectric effects, magnetostriction – 75.47.Lx Manganites 75.30.Gw Magnetic anisotropy

1 Introduction

The study of materials which show interplay between magnetism and ferroelectricity began in the 1960s [1,2]. Recently a number of diverse physical phenomena (giant magnetoresistance, giant magnetocapacitance, colossal magnetostriction etc) in multiferroic materials were discovered. This revival of interest in magnetoelectric materials

led to the discovery of new class multiferroic materials, in which the magnetic order is incommensurate (IC) with the lattice period. Due to their interesting physical properties, these compounds are promising candidates for further practical applications. Surprisingly, to this group of multiferroic materials belong compounds with very various crystallographic structures like ReMnO_3 hexagonal manganites [3,4,5], ReMn_2O_5 orthorhombic manganites [6,

7], $\text{Ni}_3\text{V}_2\text{O}_8$ compounds with Kagomé-staircase structure [8] and $\text{Ba}_{0.5}\text{Sr}_{1.5}\text{Zn}_2\text{Fe}_{12}\text{O}_{22}$ hexagonal compounds [9]. A common and essential feature of these compounds is that the frustrations in the magnetic interactions result in non-collinear spin orderings. Generally, certain types of magnetic order can lower the symmetry of the system to one of the polar groups, which allows ferroelectricity. According to the recent experimental results helical magnetic structures are the most likely candidates to host ferroelectricity. In addition, X-ray diffraction studies in a number of the above materials have revealed that the modulated magnetic structure is accompanied by structural modulation. It is, therefore, a natural assumption that lattice displacements actively participate in the formation of the ferroelectric (FE) state as well as the FE displacements. Owing to their smallness they have not been measured directly yet. This calls for theoretical microscopic models providing a mechanism by which the FE lattice displacements are induced and coupled to the IC magnetic structure. In this paper we have tried to give a theoretical explanation for our experimental results.

2 Samples and experiment

Single crystals of HoMn_2O_5 and TbMn_2O_5 were grown as described elsewhere [10]. The samples were characterized and oriented by X-ray diffraction. The magnetization measurements were realized with Foner-type magnetometer on a frequency 3.6 Hz. Cubical samples with typical dimensions data $1.2 \times 1.4 \times 1.5 \text{ mm}^3$ and weights 9.8 -13.5 mg are used. For our dielectric constant measurements

thin rectangular specimens of single domain crystals with typical area 3 - 4 mm^2 , thickness 0.3 mm and weight 7.4 - 9.2 mg were used. The dielectric constant measurements were conducted on high precision capacitance bridge AH 2550A in fields 0 - 14 T and temperatures 4.2 - 300 K. Samples polarization at fixed H and fixed T were measured using a Keithly 617 electrometer. The magnetostriction (MS) data were obtained by use of high precision capacitance dilatometer at different temperatures below 100 K in fields up to 14 T.

3 Results and Discussion

At room temperature ReMn_2O_5 single crystals have space group P_{bam} . The structure consists of edge-sharing Mn^{4+}O_6 octahedra, forming chains along the c axis, crosslinked via Mn^{3+}O_5 pyramidal units. Magnetization data for HoMn_2O_5 and TbMn_2O_5 single crystals have been acquired as a temperature dependence in range 4.2 - 120 K and as magnetic field dependence in range 0 - 14 T. Saturation of the sample magnetization in fields up to 14 T was not observed. Typical temperature dependence curves for HoMn_2O_5 and TbMn_2O_5 along the three principal crystallographic directions are shown respectively in Fig. 1 left block and Fig. 1 right block. In both compounds a significant magnetic anisotropy is presented. The values of the total magnetic moment of the compounds, derived from our measurements, are $17.4 \mu_B$ and $14.6 \mu_B$ for HoMn_2O_5 and TbMn_2O_5 respectively, which are in a good agreement with the expected ones.

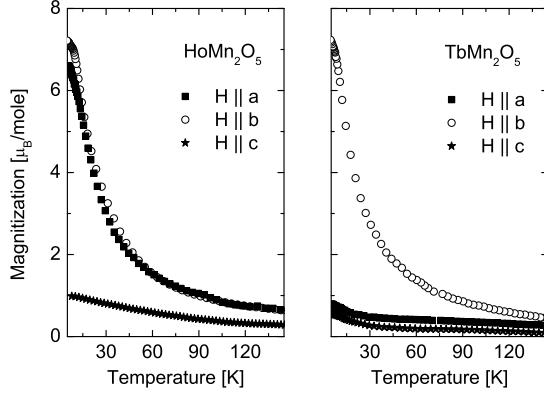


Fig. 1. Temperature dependencies of magnetization for HoMn_2O_5 and TbMn_2O_5 single crystals along the three principal crystallographic directions as following along axis **a** - square **b** - circle **c** - star

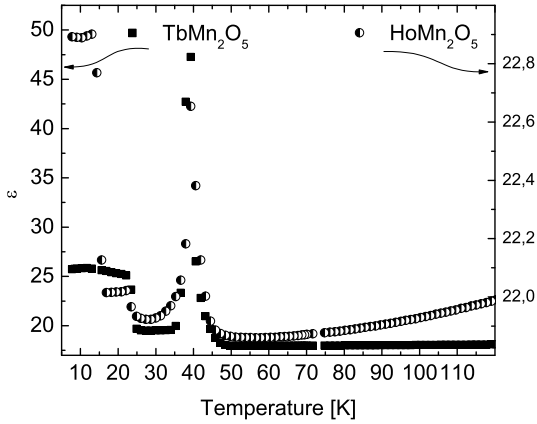


Fig. 2. Temperature dependency of dielectric constant for TbMn_2O_5 (square) and HoMn_2O_5 (circle) single crystals at 1 kHz along the **b** axis measured by sample cooling the in presence of 1 T magnetic field.

It is characteristic for all REMn_2O_5 compounds that the various magnetic phase changes are reflected in sharp and distinct anomalies of the dielectric constant, as shown for HoMn_2O_5 and TbMn_2O_5 in Fig.2. This is a clear indication for strong magneto-electric coupling due to large

spin-lattice interactions. Long-range antiferromagnetic (AFM) ordering of the $\text{Mn}^{3+}/\text{Mn}^{4+}$ spins occur at $T_N = 43$ K. This transition into a high Néel temperature phase is the common features for all REMn_2O_5 . Subsequently the FE transition takes place at T_C slightly below T_N ($T_C = 39$ K for HoMn_2O_5 and 38 K for TbMn_2O_5). The pure ferroelectric lock-in transition, observed at 39 K is not influenced by magnetic fields. With further temperature decreasing, at T'_N (22 K for HoMn_2O_5 and 24 K for TbMn_2O_5) another magnetic transition takes place, at which commensurate AFM ordering becomes low temperature incommensurate. This transition is accompanied by a significant decrease of the FE polarization and is often referred as a second FE phase transition. Under T'_N the spin wave vector remains unchanged and the transition involves an increase in the ordered moments of the $\text{Mn}^{4+}/\text{Mn}^{3+}$ sublattice. Below 19 K a phase transition to canted AFM (CAFM I) takes place in HoMn_2O_5 and TbMn_2O_5 single crystals. It was found from our measurements [10,11] that second CAFM - type ordering (CAFM II) of RE ions occurs at $T_N(\text{Ho})$ below 11 K. Measurements at low magnetic fields show peculiarities in the dielectric constant for both compounds around 11 K. The last two transitions, at $T_N(\text{Ho,Tb})$ and T'_N , change significantly their shape and place, depending on the intensity of the applied magnetic field. This is a clear indication for their magnetic origin. It has been assumed that the long-range magnetic ordering of $\text{Mn}^{3+}/\text{Mn}^{4+}$ induces the FE transition via an additional Jahn-Teller distortion of Mn^{3+} ions [12]. The FE state exhibits canted antiferromagnetic displacements

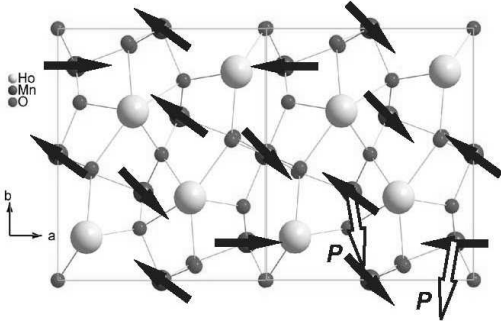


Fig. 3. Spin and dipolar moment (black and white arrows) orientation in doubled along the **a** axis ReMn_2O_5 unit cell

of the Mn^{3+} ions. These displacements lift the magnetic degeneracy by lowering the crystal symmetry to P_{b21m} , thus stabilizing the FE state via the magnetic Jahn-Teller effect. As shown on Fig 3 The spins of two Mn^{3+} per unit cell are each frustrated with two neighboring Mn^{4+} with the same spin direction. Reducing this frustration by moving the Mn^{3+} away from the Mn^{4+} generates a dipolar moment \mathbf{P} [11] between the Mn^{3+} and the surrounding oxygen ions. The \mathbf{P}_a components of this dipolar moments cancel out while the \mathbf{P}_b -components add up to the macroscopic polarization and ferroelectricity along the **b** axis. The proposed displacement lowers the symmetry to the space group P_{b21m} . The AFM modulation along the **a** axis with $\mathbf{q}_x=0.5$ leads to the frustration and displacement of both Mn^{3+} and the net polarization along the **b** axis. In the temperature range 4.2 – 43 K a consistency of magneto-elasto-electric phase transitions was observed. It was pointed out that all the ferroelectric phases are strongly tied to the antiferromagnetic $\text{Mn}^{3+}/\text{Mn}^{4+}$ spin structure, with the latter being dominated by the f-d exchange interaction [3].

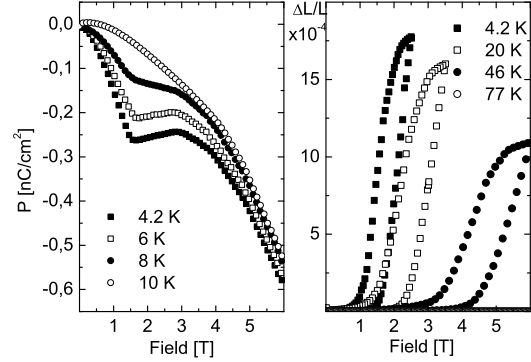


Fig. 4. Polarization (left block) and magnetostriction (right block) field dependencies measured along the **b** axis of HoMn_2O_5 single crystals

The appearance of ferroelectricity is a consequence of frustration between NN and NNN (next-nearest neighbour) Mn^{4+} in the lattice. The frustration is lifted by Jahn-Teller distortion, and the associated reduction of symmetry allows the formation of a spontaneous polarization. Considering the role of magnetic frustration to stabilize the ferroelectricity in ReMn_2O_5 there are interesting similarities to multiferroic $\text{Ni}_3\text{V}_2\text{O}_8$ and TbMnO_3 [12]. By other compounds it was shown that the transition sinusoidal to helical magnetic modulation can introduce a third order coupling giving rise to FE order [12]. On the other hand more detailed treatment shows that the existence of a spiral magnetic structure alone is not yet sufficient for FE: not all the spiral can lead to it. As shown in [13] FE can appear if the spin rotation axis \mathbf{e} does not coincide with the wave vector of a spiral \mathbf{Q} : the polarization \mathbf{P} appears only if these two directions are different and it is proportional to the vector product of \mathbf{e} and \mathbf{Q} : $\mathbf{P} \sim \mathbf{Q} \times \mathbf{e}$. However, it is not clear yet if the magnetic struc-

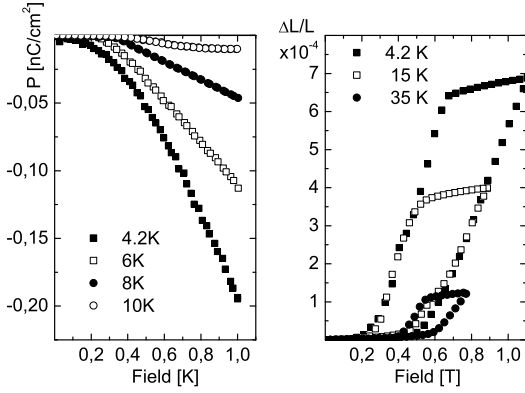


Fig. 5. Polarization (left block) and magnetostriction (right block) field dependencies measured along the **b** axis of TbMn_2O_5 single crystals

ture between T_C and T_N for HoMn_2O_5 and TbMn_2O_5 is sinusoidal and the transition into the FE phase follows the same mechanisms as in $\text{Ni}_3\text{V}_2\text{O}_8$ or TbMnO_3 . Furthermore, the magnetic modulation in the FE phase of HoMn_2O_5 and TbMn_2O_5 is commensurate whereas it is incommensurate in $\text{Ni}_3\text{V}_2\text{O}_8$ or TbMnO_3 . As discussed in [10] the reason to observe such colossal magnetostriction effect is the total effect of the exchange magnetostriction of the manganese ions and the holmium single ion magnetostriction. Holmium and Terbium in metal state showed gigantic single-ion magnetostriction [14], which is due to both, the strong spin-orbit coupling between orbital magnetic moment M_L and non-spherical charge cloud of $4f$ - electron shell (which is highly anisotropic), and strong spin-lattice interactions. When a Ho ion is placed in the crystal lattice the anisotropy of the $4f$ -electron shell remains practically unchanged. In external magnetic field the spin moment M_S changes its orientation and this leads

to reorientation of M_L . This causes a strong perturbative effect on the crystal field (the spin - lattice interactions in the HoMn_2O_5 and TbMn_2O_5 compound are strong [15]) and a colossal magnetostriction effect appears.

The polarization and magnetostriction field dependencies of HoMn_2O_5 and TbMn_2O_5 single crystals are shown on Fig. 4 and Fig. 5 respectively. As will readily be observed, especially for HoMn_2O_5 , the place of the peculiarities in polarization field dependencies and the magnetostriction phase transition at 4.2 K is nearly the same. More detailed measurements in the temperature range 4.2 - 10 K have corroborate our assumption for possible correlation between the peculiarities in polarization and the magnetostriction phase transition. Our precise magnetization measurements in this temperature range allows to observe the absence of any magnetization peculiarities for HoMn_2O_5 neither for TbMn_2O_5 . In our opinion, the observation of polarization peculiarities only below 10 K is a direct consequence of the RE (Ho,Tb) spin reorientation.

The phase diagrams build from magnetostriction (line) and polarization (circle) measurements of HoMn_2O_5 and TbMn_2O_5 single crystals are shown on Fig. 6 left and right block respectively.

The strong magnetoelectric correlation is indicated by the observation that ordering of the Mn spins modifies the dielectric function, while ferroelectric ordering leaves an imprint on the magnetic susceptibility [3]. Magnetoelastic coupling through the exchange interaction can produce improper ferroelectricity in systems with suitable symmetry. Within the underlying exchange interactions both

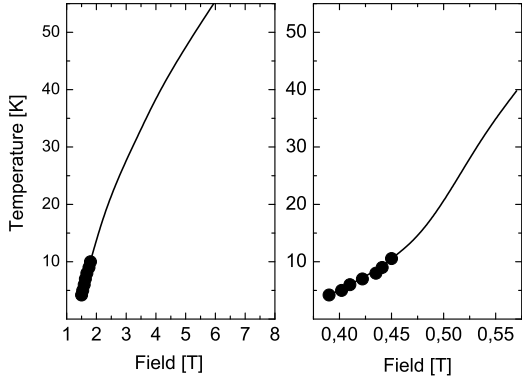


Fig. 6. Phase diagram of HoMn_2O_5 left block and TbMn_2O_5 right block single crystals built from data received by magnetostriction (solid line) and polarization (circles) measurements along the **b** axis.

symmetric and antisymmetric (or Dzyaloshinskii-Morya) type exchange can produce ferroelectricity [16,?]. The geometric magnetic frustration among the $\text{Mn}^{3+}/\text{Mn}^{4+}$ spins in REMn_2O_5 leads to a ground state degeneracy of the magnetic states. This frustration is lifted by Jahn-Teller distortion, and the associated reduction of symmetry allows the formation of a spontaneous polarization. Since this polarization is derived from canting of electric dipole moments in an antiferroelectric arrangement, denotation as 'weak' ferroelectric polarization may be used in analogy to the 'weak' ferromagnetic magnetization accompanying antiferromagnetism in the presence of a Dzyaloshinskii-Moriya interaction (DMI) [18,19]. Nowadays exist two alternative scenarios about the role of the DMI, that linearly dependent on the displacements of the oxygen ions surrounding transition metal ions, in the magnetoelectric effect in IC multiferroics. In the first one is suggested that

the DMI induces the polarization of the electronic orbitals, without the involvement of the lattice degrees of freedom [20]. The alternative scenario assert, that the DMI effect is twofold: it induces the FE lattice displacements and helps to stabilize helical magnetic structures at low temperature [21]. The distortion of perovskite lattice leads to the further-neighbor exchange interactions and non-trivial magnetic structures, like the helical spin structure observed in IC, with the lattice period magnetic order, multiferroic materials. This way the key role of the helical spin structure, induced by frustrated exchange interactions, in producing the electric polarization and enhanced magneto-electric coupling is shown.

4 Conclusions

In the present article the temperature dependencies of the magnetization and the dielectric constant, as well the field dependencies of the polarization and magnetostriction for two series of HoMn_2O_5 and TbMn_2O_5 monocrystals are discussed. As is evident, by temperature lowering these orthorhombic manganites undergo cascade phase transitions, which complexity origin in the partially competing interactions between $\text{Mn}^{3+}/\text{Mn}^{4+}$ spins, rare earth magnetic moments and the lattice [11]. We have observed also a colossal magnetostriction effect for both HoMn_2O_5 and TbMn_2O_5 monocrystals. This effect result from the re-orientation of the spin moments in external magnetic field and its strong perturbative effect on the crystal field. Compared to HoMn_2O_5 monocrystals the observed magnetostriction effect in TbMn_2O_5 monocrystals is stronger

and appears in lower magnetic fields. The same magnetostrictive behavior was observed in pure Ho/Tb monocrystals in metal state [14]. The more detailed measurements of magnetization, polarization and magnetostriction of HoMn_2O_5 and TbMn_2O_5 monocrystals in the temperature range 4.2 - 10 K give us the possibility to build the phase diagrams for both monocrystals. These diagrams clearly demonstrate the correlation between the peculiarities in polarization and the magnetostriction phase transition. In our opinion, the field couples to the magnetic order resulting in field-induced spin reorientations and magnetic phase transitions, which in turn should affect the lattice, via the spin-lattice interaction. In this way they realize the correlation observed between the polarization and magnetostriction. Knowing the signature and the nature of the magnetoelastic effect we have essential information about the intrinsic magnetoelastic and magnetoelectric interactions. To elucidate the role of the rare earth ions in this processes further investigations are necessary.

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